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Slip cast nitride-bonded silicon carbide bodies

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Abstract

The dispersion behaviour of SiC, Si and their mixtures, in deionised water, was studied as a function of pH by sedimentation, viscosity, rheology and zeta potential measurements. Slips of SiC + Si mixtures (3:1, 1:1 and 1:3 weight ratios) with 1 wt.% of Fe_2O_3 (with respect to Si), conditioned in the pH range 8–9.5 were slip cast to 56–65% dense green bodies. These on nitridation under 0.18 MPa pressure of high-purity nitrogen at 1400–1450 °C for 2–4 h resulted in nitride-bonded SiC bodies having 30–76 vol.% of Si_3N_4 bond, densities of 2.1–2.4 g cm^{-3} and 3-point flexural strengths of 60–220 MPa. The phase analyses of the products were carried out by XRD and microstructure by SEM studies. © 2002 Published by Elsevier Science B.V.

Keywords: Slip casting; Nitridation; Nitride-bonded silicon carbide; SiC–Si_3N_4

1. Introduction

Si_3N_4 and SiC ceramics have been recognised as potential candidates for high-temperature structural applications, e.g., in advanced heat engine parts, in heat exchangers, in friction and wear-resistant components, etc. [1]. However, the principal disadvantage, which limits their mechanical applications, is their marked brittleness. In a promising approach to improve the toughness of monolithic ceramic materials, Si_3N_4–SiC composites have attracted attention mainly due to their improved high temperature strength and fracture toughness [2,3]. Si_3N_4-bonded SiC ceramics (NBSC) have generated a sustained interest for their use in the field of refractories as well as for high-temperature structural applications for a long time [4–7]. Generally, NBSC products consist of 5–45 vol.% Si_3N_4 bonding phase with the remainder being the inert SiC phase. These ceramics are known to possess remarkable erosion, corrosion and chemical resistance at high temperatures as well as good thermal shock resistance and hence they find specific applications in metallurgical, chemical, ceramic and aerospace industries [7–10]. The lower cost of Si powders (compared to Si_3N_4) and the lower temperature of consolidation (nitridation) are added attractions of the reaction bonding process in addition to the near-net-shaping possibility [11,12]. Several investigators have studied the physical, chemical, mechanical and microstructural behaviour of the NBSC products [4,6,8,9,13–17]. Contrary to the NBSC products, the reaction-bonded silicon nitride (RBSN) reinforced with SiC particles or platelets, studied by few investigators [4,18–21] consists ≈5–30 vol.% of SiC phase dispersed in the RBSN matrix. Such RBSN-SiC composites are much stronger and tougher than monolithic RBSN and they retain their room-temperature properties up to 1400 °C, wherein the properties are mainly controlled by the microstructure and micro-chemistry of the interface between the matrix and the reinforcing agent. This study was focused on investigating the reaction nitridation process of colloidally processed and slip cast SiC + Si mixture compacts in the weight ratios of 3:1, 1:1 and 1:3, to develop NBSC or SiC-RBSN composites having various amounts of Si_3N_4 as bonding phase.

2. Experimental

Commercial SiC (type G1200, M/s Grindwell Norton, Bangalore, India) and Si (type RQ, M/s Keminord Industries, Norway) powders used in this study were characterised for phase purity by X-ray diffraction (XRD; X-ray Diffractometer, PM 9002, M/s Phillips, Holland). The dispersability of SiC, Si and SiC + Si mixtures in deionised water as a function of pH was investigated by studying their particle/floc size distribution, electrokinetic behaviour, sedimentation and viscosity/rheological behaviours and the details were presented elsewhere [22–24]. For slurry characterisation, the powders were dispersed in deionised water with continuous magnetic stirring (5–20 min) and the pH of the slurry was adjusted in the range 2–12 using HNO_3 for acidic and NH_4OH solution for alkaline ranges, respectively. The particle/floc size distributions of the powders (5 wt.% slurry) were measured as a function of pH, by

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using Sedigraph 5100 (M/s Micromeritics, USA). The sedimentation behaviour was studied as a function of time for 20 wt.% solid-loaded suspensions taken in long test tubes (ϕ150 mm × 13 mm). The rheological behaviour has been studied by measuring viscosity and shear stress as a function of shear rates at various pH levels and solid loadings (35–62 wt.%) by using a rotational viscometer (Viscotester, VT500, M/s Haake, Germany). The electrophoretic mobility and hence the zeta potential of SiC and Si particles (20 wt.% slurry) was measured using a mass-transport apparatus (Zeta Potential Analyser, 1202, M/s Micromeritics, USA).

Aqueous slips of SiC G1200 + Si RQ mixtures in the weight ratios of 3:1, 1:1, 1:3 and 0:1, designated as 75SCSN, 50SCSN, 25SCSN and 0SCSN (RBSN) were prepared with 1 wt.% Fe_2O_3 (with respect to Si) in deionised water using magnetic stirrer and the pH was adjusted to a optimum value (8–9.5) based on the slurry characterisation studies. The slips (≈72 wt.%) were milled in polythene jars for ≈16–20 h using Al_2O_3 balls as milling media and were then cast into plaster moulds to obtain bars (50 × (8–10) × (6–9) mm^3) and discs (25 × 10 mm^2). The green densities were derived from their weight and dimensional measurements. All slip cast bodies of SiC + Si were nitrided initially at 1400 °C for 2 h and then the temperature was increased to 1450 °C at the rate of 1 °C/min and nitridation was continued for further 2 h (total nitridation schedule = 1400 °C/2 h + 1450 °C/2 h) in a resistive graphite furnace (M/s Dynatech Engineering, Mumbai) under 0.18 MPa pressure of high-purity nitrogen (grade I, M/s Bhoruka Gases, Bangalore; max. impurities ≤8 ppm). The nitrided products were characterised by: (i) percentage of nitridation, (ii) percentage of Si_3N_4 bond formed (both from weight gain after nitridation), (iii) the nitrided density (weight/volume method) and (iv) apparent porosity (by water displacement method). The various phases formed after nitridation were analysed by XRD. The 3-point flexural strengths were measured for 6–8 rectangular bar specimens (50 × (8–10) × (6–9) mm^3) using a span width of 40 mm and cross-head speed of 0.5 mm min^{-1} in a universal testing machine (5500R, M/s Instron, UK) and the standard deviations were calculated. The microstructures of the fractured surfaces were observed in a scanning electron microscope (Leo 440, M/s Leo Electron Microscopy, UK).

3. Results and discussion

3.1. Slurry characterisation of SiC + Si mixtures

The results of the studies on particle size distribution (PSD), sedimentation, viscosity and rheological behaviour of SiC and Si slurry in aqueous media as a function of pH are in good correlation with each other [22–24]. These results reveal that pH 10 is the condition of optimum dispersion for SiC and pH 4 and 8 for Si as manifested by a shift in the PSD curve to the finer range, lower sedimentation heights,

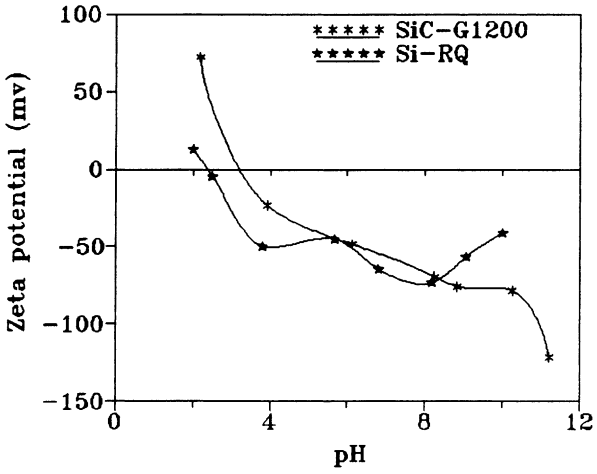

Fig. 1. Zeta potential versus pH for SiC G1200 and Si RQ.

minimum in viscosity and near-Newtonian flow behaviour. On the contrary, at other pH values the slips of SiC and Si show shifts in the PSD curves towards coarser range, higher sedimentation heights, higher viscosity and non-Newtonian flow behaviour. These properties are directly related to the zeta potential values presented in Fig. 1 as a function of pH. The zeta potential arising out of net effective surface charges on the particles directly reflects the dispersability levels of the particles in a medium. The high zeta potential values around pH 10 for SiC and around pH 4 and 8 for Si indicate the development of high surface charges around these respective pH values and hence the optimum dispersion due to inter-particle repulsion. The isoelectric points of 3.3 for SiC and 2.4 for Si represent the region of high agglomeration leading to higher sedimentation heights, higher viscosity and non-Newtonian flow behaviour for the respective slips [22–24]. The PSDs measured at the pH of optimum dispersion reveals that the SiC powder has slightly wider size distribution with $d_{10} = 0.6\,\mu m$, $d_{50} = 2.5\,\mu m$ and $d_{90} = 8.0\,\mu m$ as compared to the Si particles which show $d_{10} = 0.72\,\mu m$, $d_{50} = 2.9\,\mu m$ and $d_{90} = 4.8\,\mu m$ [24].

The sedimentation heights measured after 2 and 24 h for SiC + Si (75SCSN, 50SCSN and 25SCSN) slips are presented, respectively, in Figs. 2 and 3 as a function of pH. After 2 h of dispersion, the minimum in sedimentation heights in the pH range 5–10 indicates good dispersion, while higher sedimentation heights at extreme pH values of ≤4 and ≥10 are attributable to higher levels of agglomeration. On the contrary, after 24 h, the trend in sedimentation remained the same for 75SCSN and 50SCSN compositions, but the sedimentation minima is more pronounced around two pH values of 5 and 9 for 25SCSN composition. This shows that the dispersion and sedimentation (packing) behaviour is approaching to that shown by Si particles [23] with increasing Si content in the mixture. The viscosity values for the SiC + Si (75SCSN, 50SCSN and 25SCSN) slips measured at the shear rate of 971 S^{-1} and presented as a function of pH in Fig. 4 exhibits characteristics of both

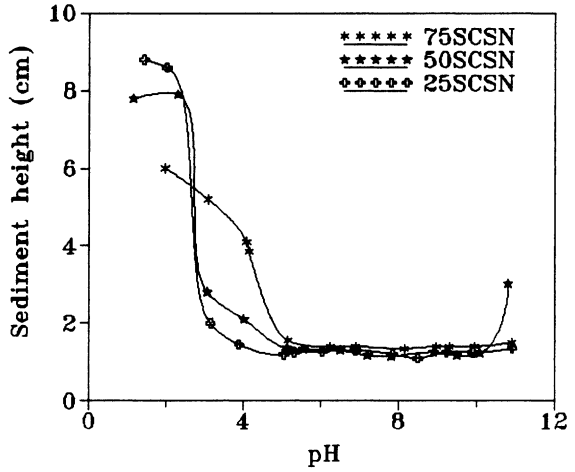

Fig. 2. Sedimentation height versus pH for SiC + Si mixtures after 2 h.

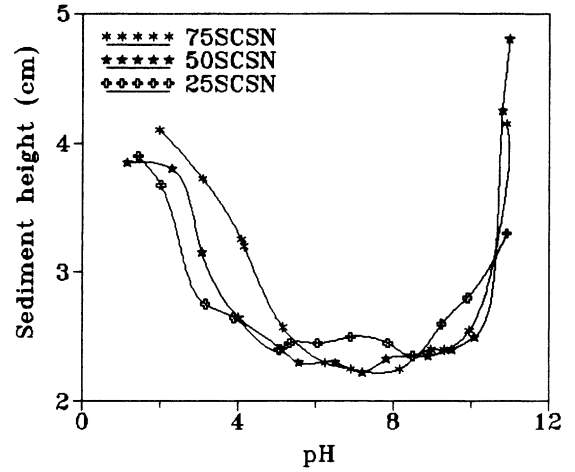

Fig. 3. Sedimentation height versus pH for SiC + Si mixtures after 24 h.

the individual components, with distinct minima around the pH values of 4–5 and 8–10 as against the pH values of 10 for SiC [22] and 4 and 8 for Si [23]. Thus, the pH values in the range 8.0–9.5 could be considered as the optimum dispersing condition for slip casting of SiC + Si mixtures.

3.2. Slip casting and nitridation of SiC + Si mixtures

The slip casting conditions of SiC + Si mixtures, their compositional density as well as the bulk density of the

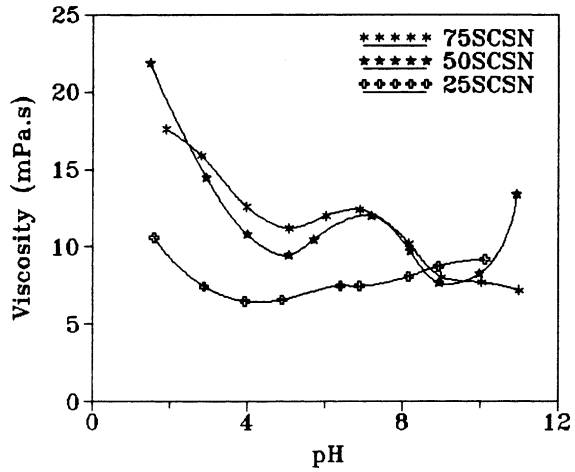

Fig. 4. Viscosity versus pH for SiC + Si mixtures in deionised water (52 wt.%) at 971 S^{-1}.

slip cast green compacts are presented in Table 1. On the average, the slip casting duration was about 10–15 min for solid casting of rectangular bar (50 × (8–10) × (6–9) mm^3) and disc (25 × 10 mm^2) specimens. The lowest green density of the 50SCSN compacts may be attributed either to the least packing efficiency of SiC and Si powders in 1:1 weight proportion or due to slight shift in the dispersion condition of the slip from the optimum, leading to partial agglomeration and higher viscosity of the slip. However, a general trend of the increase in percentage theoretical density from 58 to 67% with increase in Si content from 25 to 100% could be attributed to the better packing efficiency of Si particles as compared to that of SiC, which is also confirmed earlier by slip casting of pure SiC, Si as well as their mixtures without Fe_2O_3 additions [22–24].

Generally, the packing of the particles and the green density of the slip cast compacts are the function of the PSD and the dispersability of the powders. In this study, though a direct correlation of green density for slip cast SiC and Si compacts with the PSD of these powders is not evident, the variation in green density could be related to the dispersability of these powders in aqueous media which is controlled by the surface characteristics of the powders. In aqueous media, the Si particles are expected to produce more surface silanol groups due to oxidation and hydroxylation than SiC particles, wherein the surface hydroxylation depends upon the extent of surface silica present on the SiC particles. The

Table 1
Characteristics of slip cast SiC + Si compacts

Sample identity	Initial composition		Compositional density[a] (g cm^{-3})	Bulk density	
	SiC (wt.%)	Si (wt.%)		(g cm^{-3})	(%)
75SCSN	75	25	2.98	1.737	58.2
50SCSN	50	50	2.75	1.538	55.9
25SCSN	25	75	2.53	1.633	64.7
0SCSN (RBSN)	0	100	2.33	1.563	67.1

[a] By rule of mixtures (theoretical density of SiC = 3.2 g cm^{-3} and Si = 2.33 g cm^{-3}).

Table 2
Characteristics of SiC-RBSN composites

Sample identity	Nitridation with respect to Si (%)	Si_3N_4 formed (wt.%)	Free Si (wt.%)	SiC in the product (wt.%)	Nitrided density (g cm^{-3})	Apparent porosity (%)	MOR (MPa)
75SCSN	83.7	30.6	3.6	65.8	2.077	32.5	69 ± 10
50SCSN	89.2	57.3	4.2	38.6	2.061	33.1	119 ± 25
25SCSN	87.9	76.2	6.4	17.4	2.353	21.4	168 ± 56
0SCSN (RBSN)	73.7	81.9	18.1	–	2.359	17.9	168 ± 33

surface oxidation and hydroxylation of Si particles would be enhanced further by wet milling whereas it is less effective in the case of covalent SiC particles, leading to increased dispersion, reduced viscosity and hence increased packing and green density of the slip cast Si compacts.

The characteristics of the NBSC or SiC-RBSN composite bodies resulting from the nitridation of slip cast SiC + Si compacts are presented in Table 2. The XRD spectra of the products are presented in Fig. 5(a)–(c) and the microstructures of the fractured surfaces are depicted in Fig. 6(a)–(c). The percentage of Si_3N_4 bond formed, free Si and the SiC content of the products are in good agreement with each other. Higher percentage of nitridation was observed for SiC-RBSN composites as compared to pure RBSN bodies due to lower mass of Si to be nitrided than in monolithic RBSN. The nitrided density and the apparent porosity of

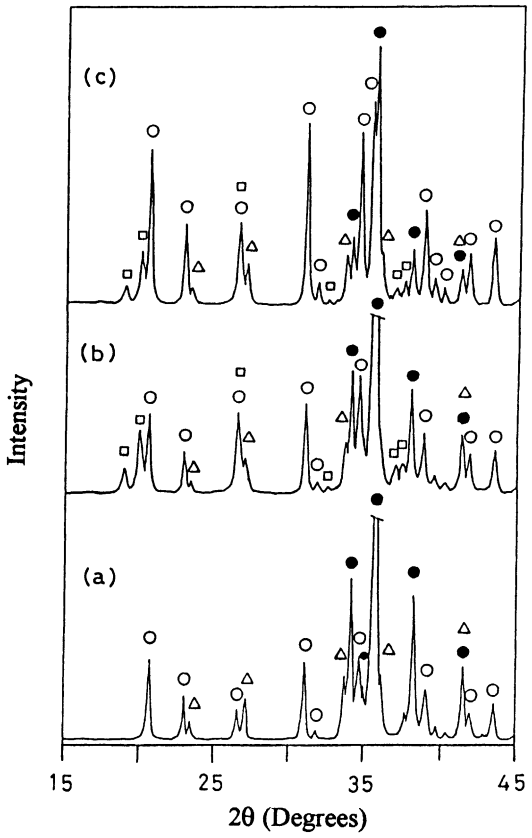

Fig. 5. XRD spectra of: (a) 75SCSN, (b) 50SCSN and (c) 25SCSN. Phases identified: (●) α-SiC; (○) α-Si_3N_4; (Δ) β-Si_3N_4; (□) Si_2ON_2.

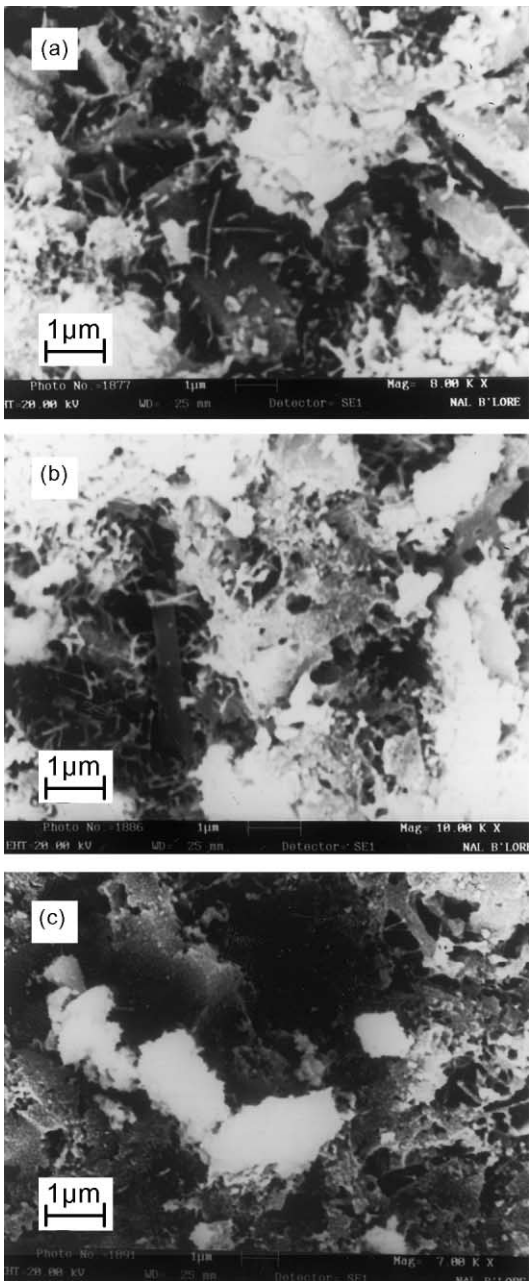

Fig. 6. SEM of fractured surfaces of SiC-RBSN composites: (a) 75SCSN, (b) 50SCSN and (c) 25SCSN.

the products are related to the green density and percentage nitridation. The 50SCSN sample in spite of near-complete nitridation (≈90%) resulted in lower nitrided density and higher apparent porosity due to its lower green density.

The mechanical properties of the above SiC-RBSN composite bodies developed by slip casting are found promising. The 3-point MOR values in the range 60–80 MPa for 75SCSN are comparable to or higher than those reported in the literature [4,6,8–10,13,14]. The strength values in the range 110–230 MPa, obtained for 25SCSN samples which contain about 17.4 vol.% of SiC as dispersed phase in the RBSN matrix are considerably higher than 85–130 MPa reported by Mukerji and Rakshit [18] for RBSN-SiC composites produced by isostatic pressing and having 5–20 vol.% SiC phase and density in the range 2.16–2.24 g cm^{-3}. Further our results are better than those reported (115 and 140 MPa) by Kosmac and Janssen [19] for composites having 20 vol.% SiC platelets processed by injection moulding and injection moulding + cold isostatic pressing, respectively. These better strength values irrespective of the considerably higher porosity (21–33%) and lower density (2.06–2.35 g cm^{-3}) could be attributed to the uniform and homogeneous microstructures of the green body wherein the formation of agglomeration has been prevented through slurry optimisation techniques. However, the large variation in strength values (110–230 MPa) of the 25SCSN samples could be attributed to the effect of critical furnace atmosphere, like high carbon activity, which leads to the formation of β-SiC on the surface layers of the samples as observed in earlier studies on the nitridation of pure Si compacts [25]. The MOR values of 119 ± 25 MPa observed for 50SCSN samples are higher than 85 MPa, reported for products (50NBSC) with similar composition produced without Fe_2O_3 addition [24]. This can be attributed to the higher percentage (89%) of nitridation, higher amount of Si_3N_4 bond (57%) and lesser amount of free Si (4%) in the 50SCSN sample as compared to 70% nitridation, 47% Si_3N_4 bond and 12% of free Si in 50NBSC sample [24]. Further, the more uniform nitridation leading to more homogeneous microstructure in SiC-RBSN samples (Fig. 6(a)–(c)), containing Fe_2O_3 might also contribute to the higher strengths. The SEM pictures reveal typical microstructures with fibre- and needle-shaped α-Si_3N_4 crystals and flaky particles of α- and β-Si_3N_4 as well as small amount of Si_2N_2O along with SiC particulate reinforcing phase.

4. Conclusions

The slips of SiC, Si and their mixtures were optimised for best dispersion in aqueous media by studying their sedimentation behaviour, viscosity, flow behaviour and zeta potential measurements as a function of pH. Using optimum dispersion conditions of pH in the range 8.0–9.5, the slips of SiC + Si in various proportions could be slip cast in plaster moulds to yield high green density (56–67%) products. The nitridation study has proved that the extent of nitridation is a function of temperature, time and the mass of Si to be nitrided. The SiC-RBSN composite bodies produced by nitridation of slip cast SiC + Si compacts having 30–76% of Si_3N_4 bonding phase showed a considerably higher 3-point MOR value of 60–220 MPa in spite of their lower bulk density (2.06–2.35 g cm^{-3}). This could make them useful for various refractory as well as high-temperature structural applications. The microstructural studies reveal a homogeneous distribution of different phases (α- and β-Si_3N_4 with dispersed α-SiC) in the composite bodies, which have contributed considerably to the higher mechanical strength of these products.

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